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Balancing the global oceanic neodymium budget: Evaluating the role of groundwater

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Abstract

The distinctly different, $\varepsilon_{Nd}(0)$ values of the Atlantic, Indian, and Pacific Oceans requires that the residence time of Nd in the ocean (i.e., τ_{Nd}) be on the order of, or less than, the ocean mixing time of ~ 500–1500 yr. However, estimates of τ_{Nd}, based on river influxes, range from 4000 to 15,000 yr, thus exceeding the ocean mixing time. In order to reconcile the oceanic Nd budget and lower the residence time by roughly a factor of 10, an additional, as yet unidentified, and hence "missing Nd flux" to the ocean is necessary. Dissolution of materials deposited on continental margins has previously been proposed as a source of the missing flux. In this contribution, submarine groundwater discharge (SGD) is examined as a possible source of the missing Nd flux. Neodymium concentrations ($n=730$) and $\varepsilon_{Nd}(0)$ values ($n=58$) for groundwaters were obtained from the literature in order to establish representative groundwater values. Mean groundwater Nd concentrations and $\varepsilon_{Nd}(0)$ values were used along with recent estimates of the terrestrial (freshwater) component of SGD (6% of river discharge on a global basis) to test whether groundwater discharge to the coastal oceans could account for the missing flux. Employing mean Nd concentrations of the compiled data base (i.e., 31.8 nmol/kg for all 730 analyses and 11.3 nmol/kg for 141 groundwater samples from a coastal aquifer), the global, terrestrial-derived SGD flux of Nd is estimated to range between 2.9×10^7 and 8.1×10^7 mol/yr. These estimates are of the same order of magnitude, and within a factor of 2, of the missing Nd flux (i.e., 5.4×10^7 mol/yr). Applying the SGD Nd flux estimates, the global average $\varepsilon_{Nd}(0)$ of SGD is predicted to be -9.1, which is similar to our estimate for the missing Nd flux (-9.2), and in agreement with the mean ($\pm$S.D.) $\varepsilon_{Nd}(0)$ measured in groundwaters (i.e., $\varepsilon_{Nd}(0)=-8.9\pm4.2$). The similarities in the estimated SGD Nd flux and corresponding $\varepsilon_{Nd}(0)$ values to the magnitude and isotope composition of the missing Nd flux are compelling, and suggest that discharge of groundwater to the oceans could account for the missing Nd flux. Future investigations should focus on quantifying the Nd concentrations and isotope compositions of groundwater from coastal aquifers from a variety of coastal settings, as well as the important geochemical reactions that effect Nd concentrations in subterranean estuaries in order to better constrain contributions of SGD to the oceanic Nd budget.
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1. Introduction

The neodymium (Nd) isotope composition of seawater varies between ocean basins (e.g., Atlantic, Indian, Pacific), in accord with the age and composition

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of surrounding continental land masses, the chief source of Nd to the ocean [1–3]. As a consequence, Nd isotopes have been used to trace the circulation and mixing of oceanic water masses, to identify sources of rare earth elements (REE) to the ocean, and to investigate biogeochemical exchange of REEs between seawater and particulate matter [4–9]. Furthermore, because authigenic and biogenic minerals inherit $^{143}Nd/^{144}Nd$ ratios that reflect the isotopic composition of the seawater within which they form [e.g., 10], Nd isotopes are extensively employed for paleoceanographic investigations [11,12]. Neodymium isotope ratios are commonly expressed in epsilon notation, $\varepsilon_{Nd}(0)$, such that:

$$\varepsilon_{Nd}(0) = \left[\frac{(^{143}Nd/^{144}Nd)_{measured}}{(^{143}Nd/^{144}Nd)_{CHUR}} - 1 \right] \times 10^4 \qquad (1)$$

where $(^{143}Nd/^{144}Nd)_{measured}$ is the isotope ratio measured in the sample and $(^{143}Nd/^{144}Nd)_{CHUR}$ is the present day Nd isotope ratio (0.512638) for CHUR (Chondritic Uniform Reservoir) [13]. Following common practice, epsilon notation is used in this contribution.

A number of unresolved questions remain concerning the oceanic Nd budget, which consequently limits our ability to confidently interpret the geochemistry of Nd in the modern oceans and, perhaps more importantly, read the paleoceanographic Nd isotope record [14]. These unresolved questions chiefly reflect the poor constraint that currently exists with regard to the magnitude and isotopic composition of Nd fluxes to the surface oceans. In particular, the combination of atmospheric and riverine fluxes of Nd to the oceans appear to be insufficient, by roughly a factor of 10, to balance the oceanic Nd budget, and preserve the observed inter- and intra-oceanic $^{143}Nd/^{144}Nd$ ratios [15–19]. The difference between the combined river and atmospheric Nd fluxes and the flux required to balance the ocean Nd budget is referred to as the "missing Nd flux", and it is estimated to be on the order of 5.4×10^7 mol of Nd/yr [14].

The origin of the missing Nd flux has attracted the attention of numerous investigators who have proposed a wide variety of possible explanations including, but not limited to, greater atmospheric fluxes of Nd, diffusive pore water fluxes enriched in REEs, release of REEs from mid-to high-salinity regions of estuaries, remineralization, and/or rapid adsorption/desorption reactions with particles [3,8,9,14,17]. However, until recently [14] the possible contribution from submarine groundwater discharge (SGD) to the missing flux was overlooked. In this contribution we demonstrate that, to

Table 1
Arithmetic mean (±S.D.) Nd isotope compositions, reported as $\varepsilon_{Nd}(0)$, and Nd concentrations (in pmol/kg) including number of analyses for the World's oceans [a]

Ocean	$\varepsilon_{Nd}(0)$ (±S.D.) [b]	n	pmol/kg (±S.D.)	n
Atlantic	−12.8±3.8	162	20.5±9.8	227
Indian				
Western and eastern basins	−6.6±2.5	71	17.7±8.1	118
Western basins [c]	−8.1±1	26	18.3±8.6	24
Pacific	−4.2±1.9	75	18.8±11.4	252
Arctic	−9.1 [d]	1	23.3±5.9	80
Global Ocean	−9.3±5	306	19.7±9.9	680

[a] Calculated using previous published data [1–9,15,19–26], and references in [27].
[b] Present day $^{143}Nd/^{144}Nd$ ratio of CHUR is 0.512638 [13].
[c] Data from Bertram and Elderfield [3].
[d] Jones Sound water, Canadian archipelago [7].

a first approximation, SGD to the oceans can account for the "missing Nd flux", and as a consequence, is likely an important component of the global oceanic Nd budget.

2. Background

2.1. Oceanic Nd enigma

The $\varepsilon_{Nd}(0)$ values of seawater (e.g., mean $\varepsilon_{Nd}(0)$ values range from −12.8 to −4.2; Table 1) are substantially less radiogenic than oceanic basalts (i.e., $\varepsilon_{Nd}(0)=+7$ to +13 for mid-ocean ridge basalts) and deep-sea hydrothermal fluxes ($\varepsilon_{Nd}(0)=+5.2\pm1.5$) [1,2,16]. These observations, along with the fact that surface waters are more radiogenic than corresponding deep waters, indicates that hydrothermal inputs from the mid-ocean ridges, and/or other deep-sea sources, are insignificant compared to continental sources of Nd to the oceans [e.g., 3,16, and references therein]. Indeed, the inter-oceanic variation in Nd isotope ratios (Table 1) chiefly reflects the composition and age of rocks that comprise the surrounding continents. Thus, for example, rivers draining Precambrian shield rocks and Paleozoic orogenic belts on either side of the Atlantic contribute relatively non-radiogenic Nd to the Atlantic Ocean, whereas the more radiogenic Nd signatures of Pacific Ocean waters reflect rivers draining the young, Cenozoic volcanic rocks that characterize the Pacific margin [4–7]. There is a general increase in oceanic $\varepsilon_{Nd}(0)$ values in the direction of deep water circulation as progressively more radiogenic Nd is added to the ocean as deep water flows from the Atlantic to the Pacific [3]. The progressive increase in $\varepsilon_{Nd}(0)$ values in the direction of deep water flow, along with the distinct

$\varepsilon_{Nd}(0)$ values of different water masses within individual oceans indicate that advective processes are also important in controlling the distribution of Nd in the oceans [3,5,6].

The distinctly different $\varepsilon_{Nd}(0)$ values of the Atlantic, Indian, and Pacific Oceans (Table 1) suggest that the oceanic residence time of Nd (i.e., τ_{Nd}) must be similar to, or less than, the mixing time of the oceans (~ 500–1500 yr) in order to preserve these distinct inter-ocean differences [9]. However, the residence time for Nd, calculated based on river fluxes, ranges from 4000 to 15,000 yr [3,15,17,18]. These estimated Nd residence times are therefore too long to preserve the inter-ocean variation in $\varepsilon_{Nd}(0)$, and should instead produce relatively homogeneous $\varepsilon_{Nd}(0)$ values for the global ocean. To reconcile this oceanic Nd enigma, an as yet unidentified additional source of Nd to the ocean is necessary [14,16,17]. The so-called "missing Nd flux" would: (1) need to be sufficient to lower the calculated residence time of Nd by approximately an order of magnitude; and (2) possess distinctly different $^{143}Nd/^{144}Nd$ ratios, on a regional scale, which are similar to local river waters draining into each ocean basin [14,18]. In order to balance the oceanic Nd budget and preserve the inter-oceanic variations in $\varepsilon_{Nd}(0)$ values, Tachikawa et al. [14] estimated the annual missing Nd flux to the surface oceans to be on the order of 5.4×10^7 mol of Nd/yr.

As mentioned above, sources of the missing Nd flux have been the subject of substantial speculation [3,9,16,17,24,28–35]. Considering atmospheric fluxes first, Greaves et al. [28] estimated an atmospheric flux of 4.4×10^6 mol of Nd/yr, which is similar to the value (2.8×10^6 mol Nd/yr) suggested by Tachikawa et al. [14]. In contrast, Jones et al. [36] argue that eolian sources of Nd to the oceans are insignificant. These authors demonstrate that the chief source of dust that settles onto the Pacific Ocean originates from Chinese loess and other continental (Asia) sources. These eolian silicates exhibit a mean ($\pm$S.D.) $\varepsilon_{Nd}(0) = -10.2 \pm 0.5$, which differs substantially from the more radiogenic $\varepsilon_{Nd}(0)$ values of Pacific Ocean waters (i.e., $\varepsilon_{Nd}(0) = -4.2 \pm 1.9$; Table 1). Moreover, they argue that leaching of Nd from settling particles must also be insignificant as Pacific surface waters are more radiogenic than deep waters [36]. After ruling out atmospheric deposition, volcanic ash, and hemipelagic sediments, Jones et al. [36] settle on near-shore river derived particulates as the chief source of particle delivered REEs to the oceans. Studies employing Nd isotopes [9,24,29] suggest, however, that the fraction of Nd in atmospheric particles that is solubilized in seawater may be greater than the

estimate determined previously [28] by measuring Nd concentrations (e.g., as much as 50% vs. $\sim 2\%$, respectively). Tachikawa et al. [14] argue that if 30% of the atmospheric dust associated Nd dissolved in seawater, the flux of Nd to the surface oceans ($\sim 4.2 \times 10^7$ mol/yr) would almost be sufficient to account for the missing Nd ($\sim 5.4 \times 10^7$ mol/yr). However, their estimated $\varepsilon_{Nd}(0)$ values for the postulated larger atmospheric Nd flux are too radiogenic for the North Atlantic Ocean (i.e., $\varepsilon_{Nd}(0) = -15$ vs. -20) and not radiogenic enough for the Pacific Ocean ($\varepsilon_{Nd}(0) = -7$ to -5 vs. -4), indicating that an increased atmospheric flux cannot account for the observed regional differences in Nd isotope sources to the oceans [14].

Bertram and Elderfield [3] constructed a multi-box, mass balance model to investigate Nd concentrations and isotopic compositions in the oceans. These authors set out to test whether the model could resolve the difference in measured $\varepsilon_{Nd}(0)$ values of the ocean with the distribution of Nd concentrations. The model was able to satisfactorily address Nd concentrations via advective fluxes, however, it was necessary to invoke complex solution-particle exchange to attain reasonable agreement between the calculated and measured inter-ocean $\varepsilon_{Nd}(0)$ variations [3]. Other researchers [9] have made similar arguments involving complex solution-particle exchange to explain the $\varepsilon_{Nd}(0)$ values. Bertram and Elderfield [3] also point out that larger Nd fluxes to the surface ocean could reconcile the Nd enigma while preserving the inter-ocean $\varepsilon_{Nd}(0)$ values; however, they argue against larger influxes based on the relatively well constrained river inputs [16] and difficulties in quantifying the atmospheric flux [14,24,28]. Although it is well known that estuaries act as sinks for riverine REEs, thus limiting riverine inputs of Nd to the ocean [e.g., 16,17], more recent studies [30–33] suggest that redissolution of particulate- or sediment-associated Nd in mid- to high-salinity regions of estuaries may represent an additional source of Nd to the oceans not accounted for in previous models. However, if the 70% of the dissolved riverine Nd flux that is estimated to be removed in estuaries were to be redissolved back into estuarine water in the mid- to high-salinity reaches of estuaries, this additional flux ($\sim 6.9 \times 10^6$ mol/yr) would only account for $\sim 13\%$ of the missing Nd flux to the oceans [14], and thus could not explain the vast majority of the missing flux.

Interaction of seawater with continental margin sediments/pore waters has also been advanced as a possible additional source of REEs to the oceans. Studies have shown that early diagenesis of shelf sediments leads to elevated pore water REE concentrations and

subsequent diffusive fluxes of REEs to the overlying water column that are comparable to local river fluxes [34,37,38]. However, even if diffusive pore water fluxes of REEs were equivalent to the effective riverine flux on a global basis, the combination of riverine and diffusive pore water fluxes would also only amount to ~13% of the missing Nd flux. Other processes occurring along continental margins such as dissolution and resuspension of continental shelf and/or slope sediments may play a role in maintaining the inter- and intra-ocean ε_{Nd}(0) variations [14,35]. Lacan and Jeandel [35] present data that supports remobilization (i.e., dissolution/resuspension) of continental margin sediments as being important towards the development of local and regional ε_{Nd}(0) differences in the oceans. These arguments are further supported by studies of Nd concentrations and isotope systematics in the northeast Atlantic Ocean, the eastern Indian Ocean, and the waters of the Indonesian archipelago [14,23–26].

2.2. Submarine groundwater discharge

One aspect of the global biogeochemical cycle of the REEs that is poorly understood, and is generally absent from most discussions of the missing Nd flux, is the impact that SGD may have on the oceanic REE budget [e.g., 14]. Studies involving radium isotopes and other tracers (^{222}Rn, CH_4) indicate that groundwater discharge to the ocean is significant, and in some cases, on the order of riverine inputs [40–42]. Furthermore, in the case of some trace elements (e.g., Ba, Sr, REE), the chemical fluxes to the oceans via SGD may even surpass that of riverine fluxes [41,43–45]. Although there is some debate as to what constitutes SGD, a recent study [40] defines SGD to include all flow of water from the seafloor into the overlying marine water column within continental margin settings notwithstanding the physical driving mechanism and the chemical composition. Consequently, SGD can range in composition from fresh to brackish to saline and be driven by numerous processes including, but not limited to, terrestrial hydraulic gradients, tidal pumping and/or wave set-up, geothermal and/or density gradients, highly pressurized groundwater flow from deep, confined aquifers, and/or evaporative/reflux cycling [40,42]. By this definition the diffusive pore water fluxes discussed above would also qualify as SGD.

Global estimates of SGD vary greatly depending on a number of factors including whether the estimates only account for freshwater of terrestrial origin or also include landward cycling of marine water (i.e., recycled seawater). Global SGD estimates of fresh, terrestrial groundwaters are reported to range between ~5 to 10% of the annual global river water discharge to the ocean, with values towards the lower end of the range (i.e., 6%) generally considered to be more reasonable [40,42]. Using a total river discharge value of 42,439 km^3/yr [16], annual terrestrial-derived fresh SGD values are estimated to range from 2122 to 4244 km^3 (2546 km^3/yr for 6%). It is important to note that estimates of the annual input of river water to the oceans reported in the literature vary between ~35,000 to 43,000 km^3/yr [40, and references therein]. We chose the estimate reported by Goldstein and Jacobsen [16] in order to be consistent with earlier investigations of global REE budgets. When brackish and saline waters are included (i.e., the "intertidal and subtidal pumps" of [40]), global estimates of SGD increase to as much as 100,000 km^3/yr, or more than double the river water inflow.

The remarkably high global SGD estimate of Burnett et al. [40] demonstrates the important role that mixing of freshwater of terrestrial origin with recycled seawater within coastal aquifers is thought to play in governing the amount of SGD to the coastal oceans. Chemical reactions that occur during sub-surface mixing of fresh (terrestrial) groundwater and seawater, as well as chemical reactions between these fluids and aquifer surfaces dramatically impact the chemical composition of the fluids eventually discharged to the coastal oceans [43–47]. Biogeochemical reactions likely to be important include, among others, carbonate mineral dissolution/precipitation resulting from changes in mineral saturation states, oxidation-reduction of Fe–Mn oxides/oxyhydroxides and subsequent trace element scavenging and/or release to solution (e.g., via reductive dissolution), ion exchange, and complexation with dissolved ligands [43–47]. As a

Table 2
Estimated atmospheric fluxes of Nd (mol/yr) and ε_{Nd}(0) values to the surface ocean

	% Surface area [a]	J_{Nd}^{Atm} (mol/yr) [b]	$\varepsilon_{Nd}(0)^{Atm}$ (n)
Atlantic	25.03	7×10^5	-12.2 ± 1.8 (26)
Indian	21.85	6.1×10^5	-13.8 [c] (1)
Pacific	49.47	1.2×10^6	-10.1 ± 0.5 (3)
Arctic	3.65	1×10^5	-9.1 [d]
Global	100	$2.8 \times 10^{6, b}$	-12.3 ± 1.6 [e] (43)

[a] Percent of global ocean surface area [48].
[b] Global flux value is from [14] and fluxes for each ocean are product of the global flux and % surface area.
[c] One analysis [49].
[d] Jones Sound water, Canadian archipelago [7].
[e] Estimated from ε_{Nd}(0) data for aerosols from Atlantic, Indian, and Pacific Oceans, and Mediterranean Sea [9,19,24,29,39,49].

consequence, the effect of such mixing and surface reactions on the loading of some trace elements (e.g., Ba, Sr, REEs) to the coastal oceans is suspected to be substantial [43–47].

3. Methods

3.1. Data acquisition and analytical techniques

Neodymium concentrations and isotope data for seawater, river waters, groundwaters, aerosols, and marine particulate matter were obtained from the literature or from previous investigations by one of the authors (i.e, KHJ). Descriptions of the analytical techniques employed to measure Nd concentrations and isotope ratios can be found in the published literature from which these data were obtained (see Tables 1–3). It should be noted that the majority of studies (∼80%) from which the groundwater Nd data were extracted represent samples filtered through 0.45 μm pore-size filters, with the remaining ∼20% filtered through 0.1, 0.2, or 0.22 μm pore-size filters. All $\varepsilon_{Nd}(0)$ values obtained from the literature that were originally calculated relative to present day $^{143}Nd/^{144}Nd$ values for CHUR of 0.511847 or 0.512636 were re-calculated to a present day value of 0.512638 [13]. All Nd concentration data generated by the authors (i.e., KHJ) were quantified on filtered (Gelman Sciences, 0.45 μm, polyether sulfone membrane) and acidified (ultrapure HNO_3; Seastar Chemicals) groundwater samples using inductively coupled plasma mass spectrometry (ICP-MS) by monitoring ^{143}Nd, ^{145}Nd, and ^{146}Nd, and using ^{115}In as an internal standard (see [27] for details). Calibration of the ICP-MS was achieved and Nd concentrations verified using a series of REE calibration standards of known concentrations (e.g., 0.1, 2, 10, 100, 250, 500, 1000 ng/kg) prepared from NIST traceable High Purity Standards (Charleston, SC). Check standards were prepared from Perkin–Elmer

multi-element solutions and were routinely monitored during analysis.

3.2. Model calculations

Because fluxes of REEs to the ocean from SGD have not been measured, and hence are not known on either a global or local basis, constructing a detailed quantitative model that can address SGD of Nd to the oceans is considered premature at the present time. Nevertheless, the possibility that groundwater plays an important role in the oceanic budget of Nd can be addressed, to a first approximation, by comparing the missing Nd flux with estimates of the SGD Nd flux to the ocean calculated using Nd data from the groundwater literature and estimates of global SGD. There are a number of important caveats to consider when estimating the SGD flux of Nd to the coastal oceans in this manner including the effects of colloids, redox reactions, and the fact that the flux of salty groundwater (i.e., recycled seawater) is likely considerably greater than the fresh, terrestrial SGD flux [40,45–47]. The combined effect of these processes on the global SGD flux of Nd is, however, difficult to constrain owing to insufficient data. Nonetheless, we show here that, at least to a first approximation, SGD is a likely source of the missing Nd flux to the oceans. In the simplified approached followed in this exercise, we treat each ocean basin (i.e., Atlantic, Indian, Pacific, and Arctic) as a separate, well-mixed reservoir of uniform Nd concentration and isotope composition. We employ the effective discharge weighted mean riverine flux and $\varepsilon_{Nd}(0)$ values of Goldstein and Jacobsen [16], and use mean Nd concentrations and $\varepsilon_{Nd}(0)$ values for groundwaters calculated from data compiled from the literature to estimate SGD Nd fluxes to the ocean.

Table 1 presents average $\varepsilon_{Nd}(0)$ values and Nd concentrations for the four major ocean basins (i.e., Atlantic, Indian, Pacific, and Arctic) obtained from the

Table 3
Summary of weighted average Nd concentrations (pmol/kg), river Nd fluxes (mol/yr), and $\varepsilon_{Nd}(0)$ of rivers draining to each ocean, as well as the global averaged from [16]

	Q (km³/yr)	Nd (pmol/kg)	J_{Nd}^{RW}	$J_{Nd}^{RW\text{-eff, a}}$	$\varepsilon_{Nd}(0)^{RW}$	$\varepsilon_{Nd}(0)^{RW\text{-eff, a}}$
Atlantic	20,323	386	7.8×10^6	2.3×10^6	−12.65	−10.9
Indian	4878	184	9×10^5	2.7×10^5	−8.8	−9.7
Pacific	13,123	198	2.6×10^6	7.8×10^5	−2.95	−3.6
Arctic	4115	150	6.2×10^6	1.9×10^5	−10.4	−10.5
Global	42,349	281	1.2×10^7	3.6×10^6	−10.2	−9 (−8.5)[b]

[a] Assuming 70% removal in estuaries.
[b] Estimate from [16].

literature. To the best of our knowledge, Nd isotope data for the Arctic Ocean have not been published. Stordal and Wasserburg [7] pointed out, however, that the $\varepsilon_{Nd}(0)$ value of Jones Sound water (−9.1) in the Canadian archipelago is substantially more radiogenic than proximal Baffin Bay water, and thus, may be characteristic of Arctic Ocean water. Consequently, we employ the $\varepsilon_{Nd}(0)$ value of Jones Sound water as a surrogate for the Arctic Ocean in our calculations. It should be noted

that the Arctic Ocean does not play a prominent role in our calculations.

Atmospheric fluxes of Nd and the corresponding $\varepsilon_{Nd}(0)$ values used in the model calculations are presented in Table 2. The global atmospheric Nd flux to the ocean (2.8×10^6 mol/yr) was estimated by Tachikawa et al. [14] assuming a total aerosol input of 9.1×10^{14} g/yr, a Nd concentration of 20 ppm for the aerosols [39,49], and dissolution of 2% of the aerosol
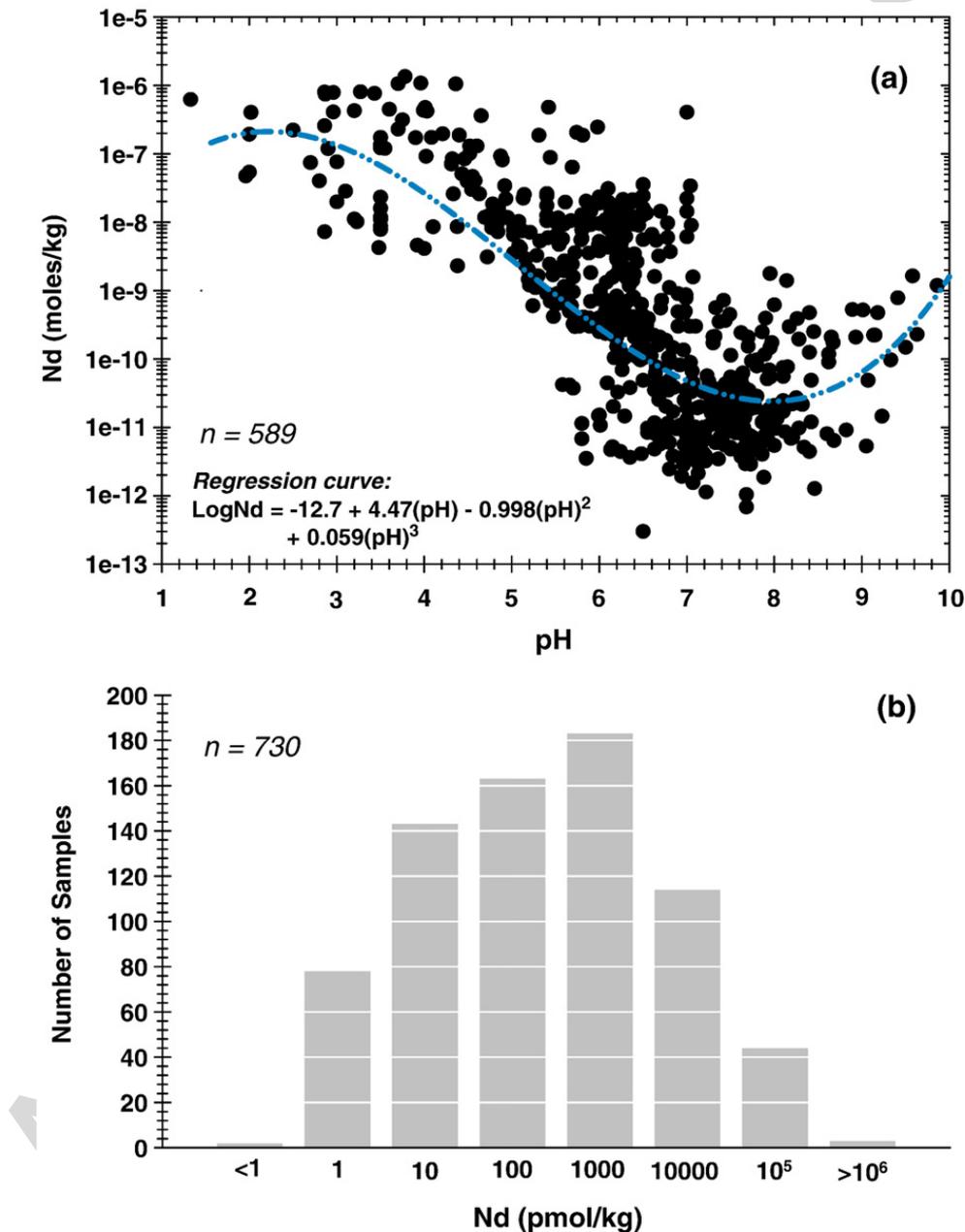

Fig. 1. Concentrations of Nd in groundwater samples as (a) function of pH and (b) histogram showing numbers of analyses within specified concentration ranges. Data are summarized from the literature [27,45,50–73]. The pH functionality of Nd concentrations can be approximated with a cubic polynomial regression equation (blue dashed line) of the form: $\log(Nd) = -12.7 + 4.47 pH - 0.998(pH)^2 + 0.059(pH)^3$. Approximately 80% of the studies from which these REE data were obtained employed 0.45 μm pore-size filters during sample processing prior to acidification and subsequent analysis. The remaining 20% of the studies used 0.1 μm, 0.2 μm, or 0.22 μm pore-size filters.

associated Nd upon contact with seawater [28]. We subsequently estimate the atmospheric Nd flux, $J_{\mathrm{Nd}}^{\mathrm{Atm},\,i}$, to each ocean ($i$ = Atlantic, Indian, Pacific, Arctic) by multiplying the global flux by the relative surface area of the global ocean occupied by each individual ocean [48]. This approach only provides a first approximation as atmospheric deposition can vary substantially, for example, as a function of distance from continental land masses [36]. The estimated $\varepsilon_{\mathrm{Nd}}(0)^{\mathrm{Atm},\,i}$ values for the atmospheric Nd flux to each ocean basin are the mean of published values of aerosols for each ocean (Table 2).

Riverine Nd fluxes and $\varepsilon_{\mathrm{Nd}}(0)$ values used in our model calculations are presented in Table 3, and are summarized from Goldstein and Jacobsen [16]. The critical values in Table 3 are the discharge-weighted, effective Nd flux, $J_{\mathrm{Nd}}^{\mathrm{RW-eff}}$, and the associated Nd isotope composition, $\varepsilon_{\mathrm{Nd}}(0)^{\mathrm{RW-eff}}$, entering the ocean. The effective river flux of Nd is determined by assuming that 70% of the riverine Nd is removed from solution in estuaries [3,16]. The global $\varepsilon_{\mathrm{Nd}}(0)^{\mathrm{RW-eff}}$ value (i.e., −8.5) is weighted to the discharge of all rivers studied by Goldstein and Jacobsen [16], whereas our estimate (−9) is weighted to the effective river water fluxes of Nd contributing to each ocean (Table 3).

Using the data presented in Tables 1–3, Nd fluxes are calculated as:

$$J_{\mathrm{Nd}}^{i} = \sum_{i} Q^{i} C_{\mathrm{Nd}}^{i} \qquad (2)$$

where Q^{i} is the volumetric discharge or flux, C_{Nd} is the Nd concentration, and i refers to specific reservoirs such as individual ocean basins, the global ocean, the atmosphere, rivers, or groundwater. The Nd isotope composition of these fluxes is determined by:

$$\varepsilon_{\mathrm{Nd}}(0)^{i} = \frac{\displaystyle\sum_{j \neq i} J_{\mathrm{Nd}}^{j \rightarrow i} \cdot \varepsilon_{\mathrm{Nd}}(0)^{j}}{\displaystyle\sum_{j \neq i} J_{\mathrm{Nd}}^{j \rightarrow i}} \qquad (3)$$

where the numerator is the sum of all Nd fluxes and corresponding Nd isotope compositions contributing Nd to reservoir i, and the denominator is the Nd flux into the reservoir [14,16].

We compare our model calculations to the calculated influxes from external sources to the surface ocean determined by Tachikawa et al. [14]. Using a 10-box model for the global ocean, a global ocean Nd inventory of 3×10^{10} mol, and the assumption that the oceanic residence time of Nd is less than the ocean mixing time, these researcher determined that an annual global external

flux (i.e., F_{i}^{ext}) of $\sim 6 \times 10^{7}$ mol of Nd was required to balance the ocean Nd budget. The difference between the total external flux and the sum of the effective riverine and atmospheric Nd fluxes provides an estimate of the missing global Nd flux (i.e., 5.4×10^{7} mol/yr). Here, we compare our estimates of the SGD Nd flux to the missing Nd flux in order to evaluate whether SGD can account for the missing flux. As an exercise, we also approximate missing Nd fluxes to each ocean basin (i.e., Atlantic, Indian, Pacific, and Arctic) using the same approach. It is critical to stress, however, that although we provide estimates for each ocean basin, we focus here on the global Nd fluxes and corresponding $\varepsilon_{\mathrm{Nd}}(0)$ values in evaluating the significance of SGD as a source of the missing Nd.

To estimate the flux of Nd to the oceans resulting from SGD, we use a conservative approach employing an estimate of the terrestrial, "freshwater" component of SGD (i.e., 6% of river discharge [40]) in combination with published Nd data for groundwaters. As mentioned above, we compiled a data base of Nd concentrations (n = 730) and $\varepsilon_{\mathrm{Nd}}(0)$ values (n = 58) for groundwaters from the published literature (Figs. 1 and 2). These data were subsequently employed to estimate representative Nd concentrations and isotope compositions for model groundwaters discharging to the ocean. As a first approximation, we use the mean Nd concentration and $\varepsilon_{\mathrm{Nd}}(0)$ value of the entire data set. In addition, we separately employ the mean Nd concentration of 141 analyses of groundwaters from a coastal aquifer in South Carolina, USA [45,67]. To the best of our knowledge, these are the only published REE data for an aquifer in direct hydraulic contact with the ocean. We recognize that actual SGD will likely exhibit a range of Nd concentrations and $\varepsilon_{\mathrm{Nd}}(0)$ values owing to complex biogeochemical reactions occurring in subterranean estuaries (e.g., colloid coagulation, scavenging by Fe/Mn oxides) and seawater cycling through coastal aquifers [45].

4. Results and discussion

4.1. Groundwater Nd concentrations and $\varepsilon_{Nd}(0)$ values

Neodymium concentrations for groundwater samples obtained from the literature are plotted in Fig. 1 as a function of pH and as a histogram showing the total numbers of samples within specific concentration ranges. Because a number of analyses (141 samples) did not include accompanying pH data, the total number of samples plotted on panels a and b of Fig. 1 differ by this value. For the Nd data plotted in Fig. 1a, the mean of these 589 analyses is 33.5 nmol/kg, whereas the mean for all 730 groundwater analyses (589 + 141; Fig. 1b) is
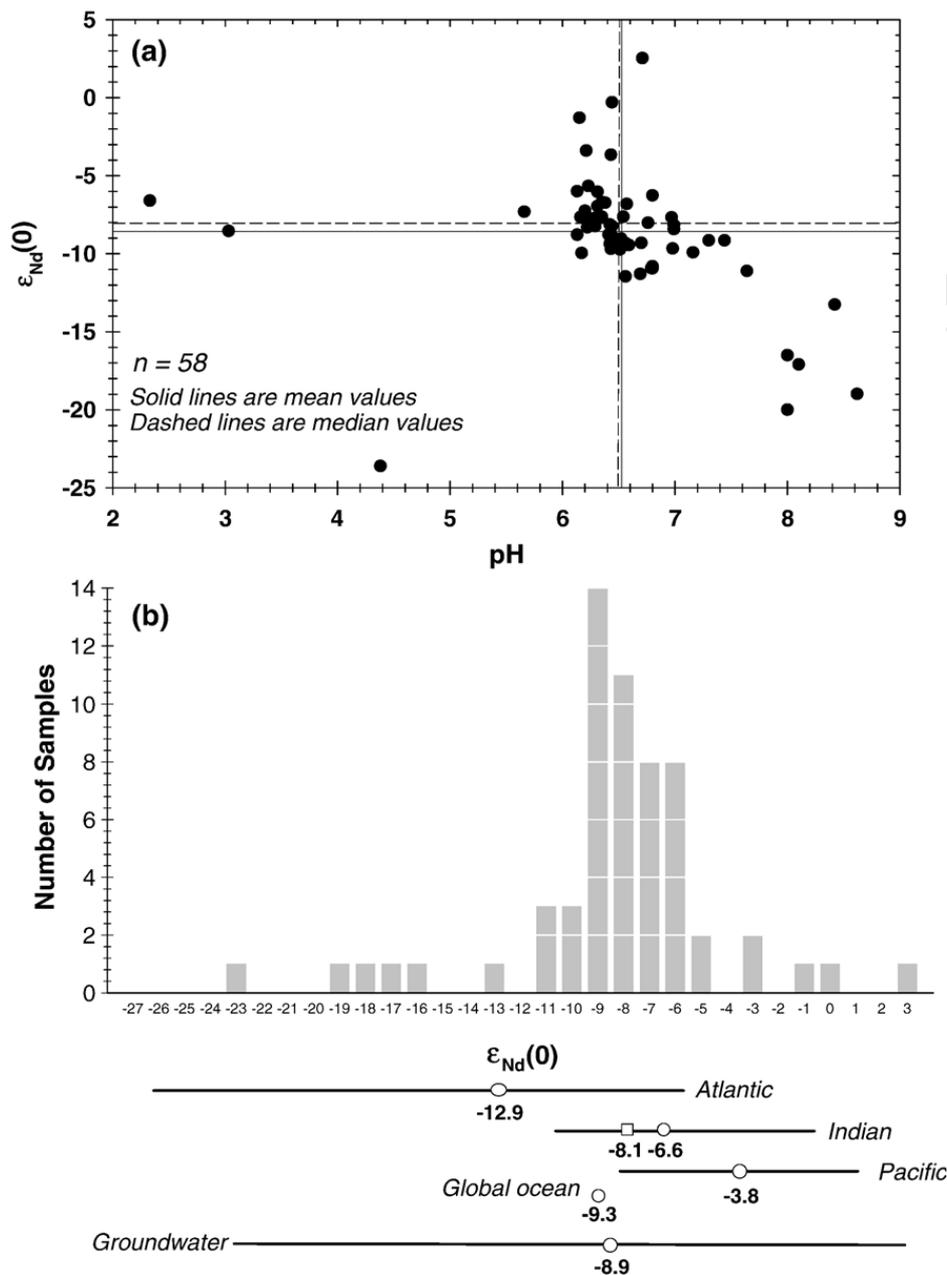
Fig. 2. Groundwater $\varepsilon_{Nd}(0)$ values summarized from the literature [54,63,64,75–77]. Panel (a) shows groundwater $\varepsilon_{Nd}(0)$ values plotted as a function of pH, whereas panel (b) depicts a histogram of the $\varepsilon_{Nd}(0)$ distribution among the groundwater sample analyses. In addition, the range and mean ε_{Nd} (0) values for the Atlantic, Indian, and Pacific Oceans, the global ocean, and the range and mean for the groundwater samples are also shown. For the Indian Ocean, the mean $\varepsilon_{Nd}(0)$ for samples from the western basins [3], −8.1, is shown along with the mean calculated with these data and more recent data from the eastern Indian Ocean [25,26].

31.8 nmol/kg. The 141 samples from the coastal aquifer along the South Carolina coast have a mean Nd concentration of 11.3 nmol/kg.

To a first approximation groundwater Nd concentrations exhibit an inverse relationship with pH such that Nd concentrations decrease with increasing pH (Fig. 1a). This inverse relationship has been recognized and reported in previous studies [e.g., 16,17]. An outstanding feature exhibited by the groundwater Nd data is that for pH >8, Nd concentrations increase with increasing pH (Fig. 1a). The increase in Nd concentrations with increasing pH in alkaline groundwaters likely reflects the stabilizing effect of solution complexation of Nd with carbonate ions and/or organic ligands, which act to enhance REE concentrations in natural waters [18,45,50,56,74]. The pH dependence of Nd can be approximated by a cubic polynomial regression curve of the form $\log(Nd) = -12.7 + 4.47(pH) - 0.998$

$(pH)^2 + 0.059(pH)^3$, where (Nd) is the concentration (Fig. 1a).

Fig. 2 presents Nd isotope data for groundwaters obtained from the literature plotted as a function of pH and as a histogram that shows the frequency of sample analyses with specific $\varepsilon_{Nd}(0)$ values. The $\varepsilon_{Nd}(0)$ values range from -23.6 to $+2.5$, and exhibit a mean ($\pm$S.D.) of -8.9 ± 4.2. The range and mean $\varepsilon_{Nd}(0)$ values for the groundwater samples are compared to the range and mean values of the Atlantic, Indian, and Pacific Oceans, and the global ocean in Fig. 2b. The range in $\varepsilon_{Nd}(0)$ values for the groundwater samples is similar to that of the global ocean, albeit, shifted to slightly more radiogenic values. The small shift in $\varepsilon_{Nd}(0)$ values of groundwaters compared to the global ocean may reflect the fact that many of the groundwater samples are from aquifers composed of Phanerozoic rocks [63].

An interesting feature of the $\varepsilon_{Nd}(0)$ data is that the bulk of the analyses for circumneutral to alkaline pH groundwaters appear to exhibit a relationship with pH (Fig. 2a). Specifically, as pH increases from 6 to 9, the $\varepsilon_{Nd}(0)$ values become progressively less radiogenic (Fig. 2a). As is the case with other natural waters, the $\varepsilon_{Nd}(0)$ of groundwaters should reflect the age and isotopic composition of the chief source of Nd to the water, which in the case of groundwaters are aquifer rocks, minerals, and/or organic matter [1,7,16,63]. Thus, to a first approximation, changes in water chemistry (i.e., pH) and other biogeochemical reactions are not expected to affect the Nd isotope composition of groundwater [16]. Closer inspection of the $\varepsilon_{Nd}(0)$ data in Fig. 2 reveals that the majority of the more radiogenic

groundwaters with pH values between 6 and ~ 7.5 are from aquifers composed of Phanerozoic rocks of the Massif Central in France, whereas the non-radiogenic groundwaters with pH >8 are from fractured Proterozoic rocks in Finland [63,64]. The groundwater sample with the lowest $\varepsilon_{Nd}(0)$ value (-23.6), and which is relatively acidic (pH ~ 4.4), is from a region of central African underlain by the late Archean Congo Craton [76]. Hence, although sparse, the available groundwater data do not support a pH functionality for $\varepsilon_{Nd}(0)$.

In summary, the data in Figs. 1 and 2 demonstrate that concentrations of REEs in groundwaters are controlled to a large degree by solution composition [e.g., 16–18,50,56], whereas the Nd isotope composition reflects the composition, and in particular, the age of the aquifer rocks/minerals [63,64]. Hence, $\varepsilon_{Nd}(0)$ values should prove to be more powerful tracers of groundwater flow, mixing, and water-rock reactions than input-normalized REE fractionation patterns.

4.2. Groundwater Nd fluxes to the ocean

The results of the model calculations described in Section 3.2 are reported in Table 4. Using the overall mean Nd concentration of 31.8 nmol/kg from the compiled groundwater Nd data base ($n=730$) as an estimate of the global average Nd concentration of groundwater, and assuming that SGD amounts to 6% of river discharge to the ocean on a global basis [40], a global SGD Nd flux of 8.1×10^7 mol/yr is estimated. By comparison, when the mean Nd concentration of the coastal groundwaters from South Carolina (i.e.,

Table 4
Comparison of estimated groundwater (GW) Nd fluxes and Nd isotope compositions to the ocean and the missing Nd flux [14]

	$J_{Nd}^{ext,a}$	$J_{Nd}^{RW-eff} + J_{Nd}^{Atm}$	$J_{Nd}^{missing,b}$	$\varepsilon_{Nd}(0)^{missing,c}$	$J_{Nd}^{GW-all,d}$	$\varepsilon_{Nd}(0)^{GW-all,e}$	$J_{Nd}^{GW-coast,d,f}$	$\varepsilon_{Nd}(0)^{GW-coast,e}$	Nd[g] (nmol/kg)
Atlantic	1.5×10^7	3×10^6	1.2×10^7	-13.2	3.9×10^7	-12.9	1.4×10^7	-13.2	9.8
Indian	1.3×10^7	8.8×10^5	1.2×10^7	-6.6 (-7.9)[h]	9.3×10^6	-6.3 (-7.9)[h]	3.3×10^6	-5.8 (-7.5)[h]	41
Pacific	3×10^7	2.2×10^6	2.8×10^7	-3.9	2.5×10^7	-4	8.9×10^6	-3.7	35.6
Arctic	2.2×10^6	2.9×10^5	1.9×10^6	-9	7.8×10^6	-9.1	2.8×10^6	-9	7.7
Global	$6 \times 10^{7,a}$	6.4×10^6	$5.4 \times 10^{7,b}$	-9.2	8.1×10^7	-9.2	2.9×10^7	-9.0	21.2

[a] Model estimate for global external Nd flux (mol/yr) to surface ocean from [14]. Values for each ocean estimated based on the percentage of global ocean surface area occupied by each [48].

[b] $J_{Nd}^{missing} = J_{Nd}^{ext} - (J_{Nd}^{RW-eff} + J_{Nd}^{Atm})$. All fluxes in mol/yr.

[c] $\varepsilon_{Nd}(0)^{missing,\, i} = (\varepsilon_{Nd}(0)^i \cdot J_{Nd}^{ext,i} - \varepsilon_{Nd}(0)^{RW-eff,\, i} \cdot J_{Nd}^{RW-eff,\, i} - \varepsilon_{Nd}(0)^{Atm,i} \cdot J_{Nd}^{Atm,i}) / J_{Nd}^{missing,\, i}$, where i = Atlantic, Indian, Pacific, Arctic, or the Global ocean.

[d] SGD assumed to be 6% of river discharge [40] to each ocean basin (i.e., Atlantic, Indian, Pacific, Arctic) and the global ocean (Table 3), and using a Nd concentration of 31.8 nmol/kg, which is the mean Nd concentration determined from the groundwater (GW) data displayed in Fig. 1.

[e] $\varepsilon_{Nd}(0)^{GW,\, i} = (\varepsilon_{Nd}(0)^i \cdot \sum J_{Nd}^i - \varepsilon_{Nd}(0)^{RW-eff,\, i} \cdot J_{Nd}^{RW-eff,\, i} - \varepsilon_{Nd}(0)^{Atm,i} \cdot J_{Nd}^{Atm,i}) / J_{Nd}^{GW,\, i}$, where i is the same as for c, and $\sum J_{Nd}^i = J_{Nd}^{RW-eff,\, i} + J_{Nd}^{Atm,i} + J_{Nd}^{GW,\, i}$.

[f] SGD assumed to be 6% of river discharge [40] to each ocean basin (i.e., Atlantic, Indian, Pacific, Arctic) and the global ocean (Table 3), and using a Nd concentration of 11.3 nmol/kg, which is the mean Nd concentration of groundwaters from a coastal aquifer from the South Carolina coast [45,67].

[g] Nd concentration required for SGD of 6% river discharge to account for the missing Nd flux.

[h] Using $\varepsilon_{Nd}(0)^{Indian} = -8.1$ [3].

11.3 nmol/kg, $n = 141$) is used in the calculation, an estimate of 2.9×10^7 mol/yr of Nd delivered to the ocean on a global scale is obtained (Table 4). These estimates of the SGD Nd flux are of the same order of magnitude as the missing global Nd flux (5.4×10^7 mol/yr). The global SGD Nd flux estimated using the mean Nd concentration of the entire groundwater data base (8.1×10^7 mol/yr) is a factor of 1.5 larger than the missing Nd flux, whereas the SGD Nd flux estimated using the coastal groundwaters (2.9×10^7 mol/yr) is less than a factor of 2 lower than the missing Nd flux. Thus, our first approximations of the global SGD Nd flux bracket the missing Nd flux, differing from the missing flux by less than a factor of 2.

Because the majority of REE data for groundwater reported in the literature and used in our calculations were filtered through 0.45 µm pore-size filters, the possibility that colloids account for substantial fractions of Nd cannot be ruled out. In seawater, the bulk of the Nd inventory is thought to be in solution (i.e., <0.45 µm) and not colloidal [3,15,18]. Although important, in the absence of high organic matter concentrations the effects of colloids on REEs in river waters is likely minimal compared to groundwaters where colloids can account for substantial fractions of aqueous REEs [45,60]. Nevertheless, studies clearly demonstrate that, on average, ∼70% of the river borne REE load is removed in estuaries owing to colloid coagulation processes [16,30,31]. The "effective river flux" employed in our model calculations takes into consideration estuarine removal by colloid coagulation [16]. If we similarly assume that ∼70% of Nd in SGD is removed within subterranean estuaries by colloid coagulation and/or other processes (e.g., adsorption, scavenging by metal oxides), we arrive at SGD Nd fluxes of 8.7×10^6 to 2.4×10^7 mol/yr. These SGD Nd flux estimates are a factor of 6 and 2 lower, respectively, than the missing Nd flux. Thus, even accounting for similar amounts of REE removal within subterranean estuaries as reported for surface estuaries results in SGD Nd fluxes that can account for at least 20% or more of the missing Nd flux.

As alluded to above, redox reactions involving Fe and/or Mn oxides/oxyhydroxides also likely exert important controls on the SGD flux of Nd to coastal oceans. Charette and Sholkovitz [47], for example, show that substantial removal of dissolved Fe occurs in a subterranean estuary beneath Cape Cod, Massachusetts, as reducing, terrestrial groundwaters encounter oxidizing, recycled seawater. The oxidation and removal of Fe in the subterranean estuary is expected to scavenge REEs from solution, possibly decreasing the SGD flux

of Nd to the coastal oceans. It is important to note, however, that Duncan and Shaw [45] present evidence of a significant REE source in the subterranean estuary, which they attribute to oxidation of organic matter and regeneration of a solid, REE-enriched phase in the aquifer sediments as seawater is recycled through the coastal aquifer. These observations suggest that recycling of seawater through coastal aquifers may diminish the net removal of REEs as terrestrial groundwaters move to the coastal ocean, and potentially may enhance the SGD flux of Nd to the coastal oceans over that originating from the fresh, terrestrial groundwater component. Hence, our results may underestimate the SGD flux of Nd to the oceans, especially in those estimates that assume 70% removal of Nd in subterranean estuaries. Without additional data it is difficult to evaluate the importance of Nd removal from SGD owing to colloid coagulation and redox-related scavenging versus that remobilized from aquifer sediments as seawater is recycled through coastal aquifers. Consequently, we are somewhat limited to a simplified approach that does not explicitly address these processes. In addition to measuring SGD fluxes, and the Nd concentrations and isotopic compositions of these fluxes, future investigations should establish whether Nd removal in subterranean estuaries via colloid coagulation and scavenging by precipitating Fe/Mn oxides/oxyhydroxides is balanced or exceeded by remobilization of Nd from aquifer sediments by salty groundwaters of marine origin.

Given the range of Nd concentrations reported for groundwaters (Fig. 1), and our conservative choice to employ the global estimate of freshwater SGD (6% of river discharge), the similarities in the missing Nd flux and our estimated SGD Nd fluxes are nonetheless compelling. These estimates of the SGD Nd flux to the global ocean strongly suggest that groundwater discharge to the coastal ocean could account for the missing Nd flux. The agreement also indicates that Tachikawa et al.'s [14] estimate of the missing Nd flux is reasonable.

Table 4 also provides estimates of the Nd isotope composition of the missing Nd flux and that of SGD, again assuming that SGD amounts to 6% of the river discharge to the ocean. Our estimates of the $\varepsilon_{Nd}(0)$ value of the global SGD Nd flux (i.e., −9.2 to −9) are similar to our estimate of the $\varepsilon_{Nd}(0)$ composition of the missing Nd flux (−9.2). In addition, the $\varepsilon_{Nd}(0)$ values of the missing Nd flux and the estimated SGD Nd flux are identical, within error, to the mean groundwater $\varepsilon_{Nd}(0)$ value calculated from the compiled data base (−8.9± 4.2; Fig. 2). Moreover, the estimate of $\varepsilon_{Nd}(0)$ for the

missing Nd flux determined by Tachikawa et al. [14], i.e., −8.6, is also identical, within error, to the mean ε_{Nd}(0) value for groundwaters from the compiled data base (Fig. 2). It should be noted that our estimate of ε_{Nd}(0) for the missing Nd flux differs slightly (i.e., 6.5%) from that of Tachikawa et al. [14] owing to differences in how we partitioned the global ocean (i.e., Atlantic, Indian, Pacific, Arctic vs. the 10 box model of [14]). Nevertheless, the similarities in the ε_{Nd}(0) values of the missing Nd flux, the predicted ε_{Nd}(0) values of the global SGD Nd fluxes, and the actual Nd isotope composition of groundwaters reported in the literature strongly points towards SGD as the source of the missing Nd flux, and hence, as an important component of the global oceanic Nd budget.

The last column of Table 4 presents the Nd concentration that would be required for SGD amounting to 6% of the global river discharge to account for the missing Nd flux. The required Nd concentration (i.e., 21.2 nmol/kg) is intermediate between the mean Nd concentration calculated using the entire groundwater Nd data base (31.8 nmol/kg), and that of the coastal groundwaters (11.3 nmol/kg). If, on the other hand, ∼70% of Nd is removed in subterranean aquifers, the pre-removal Nd concentration in the terrestrial component of SGD required to balance the oceanic Nd budget would be 71 nmol/kg, which exceeds Nd concentrations reported for terrestrial groundwaters from a coastal aquifer [67]. However, accounting for recycling of seawater in coastal aquifers, Burnett et al. [40] suggest that global SGD may be as much as 100,000 km³/yr, which is more than double the global river discharge. A flux of this magnitude would only require a Nd concentration of 0.54 nmol/kg to account for the missing Nd flux. Clearly, more data are required to better constrain the importance of SGD to the overall oceanic Nd budget.

Table 5 presents oceanic Nd residence times, τ_{Nd}, calculated based on the flux estimates in Table 4. Specifically, the Nd residence times are calculated assuming a global oceanic Nd inventory of 3×10^{10} mol [16] and the sum of effective riverine Nd flux, atmospheric Nd flux, and the estimated SGD Nd fluxes. The oceanic residence time for Nd using the estimates of the SGD Nd flux range from 340 to 850 yr (average τ_{Nd}=600 yr; Table 5), which are shorter than, or similar to, the oceanic mixing time, and hence, are of the right magnitude to preserve the inter-ocean variation of ε_{Nd}(0) values. The oceanic residence time of Nd calculated using the estimated SGD Nd fluxes agree well with those of recent investigations [14,20,24].

To summarize, the results of our analysis of the available groundwater Nd concentration and isotope

Table 5
Oceanic residence times for Nd estimated assuming SGD amounts to 6% of river discharge to the oceans

	Volume (km³)	Nd inventory (moles)	τ_{Nd} [a] (years)
Atlantic	3.4×10^{8} [b]	7×10^{9} [c]	170–410
Indian	3×10^{8} [b]	5.3×10^{9} [c]	290–440
Pacific	7.3×10^{8} [b]	1.4×10^{10} [c]	520–1260
Arctic	1.4×10^{7} [b]	3.4×10^{8} [c]	30–60
Global	13.9×10^{8} [d]	3×10^{10} [d]	340–850

[a] Range calculated based on estimates of SGD Nd fluxes from Table 4 (i.e., 2.9×10^{7} or 8.1×10^{7} mol/yr) and the sum of the effective riverine and atmospheric fluxes.
[b] Based on volume percent of each ocean [48].
[c] Using mean Nd concentrations for each ocean and the global ocean from Table 1.
[d] Goldstein and Jacobsen [16].

data, in conjunction with the estimates of global SGD Nd fluxes and corresponding ε_{Nd}(0) values, strongly suggest that groundwater discharge to the coastal ocean is the source of the missing Nd flux. Moreover, the oceanic residence time of Nd calculated using our estimates of the SGD Nd flux to the ocean also demonstrate that SGD of Nd to the oceans is, to a first approximation, of the right order of magnitude to lower previous estimates of the oceanic residence time of Nd by roughly an order of magnitude, thus preserving the variations in ocean Nd isotope composition. Consequently, our initial analysis of the available groundwater Nd concentration and isotope composition data indicates that future studies directed at resolving the oceanic Nd enigma should focus on quantifying the contributions from SGD.

4.3. Implications for paleoceanography

An underlying assumption in our Nd flux and oceanic residence time calculations is that the global hydrologic cycle is at steady-state [78]. Although this assumption is approximately valid for the short-term, it is clearly untenable over geologic time scales. As a consequence of plate tectonics, the shifting of continents and ocean basins throughout Earth history has demonstratively altered ocean circulation patterns, and hence global climate, which in turn impacts the global hydrologic cycle [79]. A severe example of the plate tectonics-global climate link is the series of Neoproterozoic glaciation events (i.e., the so-called Snowball Earth) that accompanied the break-up of the supercontinent Rodinia [80]. The application of Nd isotopes in the study of paleoceanography/paleogeography assumes that the bulk of the Nd delivered to the oceans occurs via rivers

draining the continents [16,17]. However, the oceanic Nd enigma indicates that the effective riverine flux of Nd to the modern oceans is insufficient to account for the inter-ocean variations in reported $\varepsilon_{Nd}(0)$ values. Furthermore, our preliminary analysis suggests that SGD may be the chief source of Nd to the modern ocean, exceeding the effective riverine flux by as much as 2 to 23 times. As the relative amounts of groundwater and river water discharging to the oceans can fluctuate with changing climate [78], it is reasonable to expect that the proportions of groundwater-to river-derived Nd discharging to paleo-oceans varied throughout geologic time. Consequently, although the Nd isotope signature of authigenic and biogenic minerals likely record the $^{143}Nd/^{144}Nd$ ratios of the paleo-seawater within which they formed, the Nd isotope composition of the paleo-seawater reflects the relative importance of groundwater-derived versus river-derived Nd to the surface ocean at that specific point in the geologic record [14]. Without a better understanding of how SGD effects the Nd isotope composition of the modern ocean, it is difficult to ascertain its impact on paleo-ocean $\varepsilon_{Nd}(0)$ values. Consequently, evaluating the effect that varying proportions of groundwater-versus river-derived Nd may have on interpreting paleo-ocean circulation patterns and/or paleo-geography from the geologic record will require detailed investigations of the Nd concentrations, isotope compositions, and magnitudes of SGD Nd fluxes to the modern ocean.

5. Conclusions

Groundwater Nd concentration and $\varepsilon_{Nd}(0)$ data are employed to test whether submarine groundwater discharge (SGD) to the ocean can account for the missing Nd flux, and therefore, balance the oceanic Nd budget. The necessity of an additional Nd flux (i.e., in addition to river influxes) to the ocean stems from the fact that calculated oceanic residence times for Nd exceed the mixing time of the ocean. We show that to a first approximation, SGD can account for the missing Nd flux. Using average Nd concentrations of published groundwater data (31.8 nmol/kg for 730 analyses; 11.3 nmol/kg for 141 groundwater samples from a coastal aquifer) and a conservative estimate of the global SGD to the ocean (6% of river discharge), we demonstrate that the resulting SGD Nd fluxes (2.9×10^7 to 8.1×10^7 mol/yr) are within a factor of 2 of the estimated missing Nd flux (5.4×10^7 mol/yr). Furthermore, using the flux estimates we calculate an $\varepsilon_{Nd}(0)$ value of -9.1 for the SGD Nd flux, which is consistent with the predicted values for the missing Nd flux, and identical to the mean ($\pm$S.D.) $\varepsilon_{Nd}(0)$ value of groundwater

samples reported in the literature (i.e., $\varepsilon_{Nd}(0) = -8.9 \pm 4.2$). Applying the estimated SGD Nd fluxes, an average oceanic residence time of 600 yr is determined for Nd.

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